



# Impact of welan gum stabilizer on the dispersing performance of polycarboxylate superplasticizers

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## ABSTRACT

Welan gum, a microbial biopolymer produced *via* fermentation, represents a common stabilizer (VMA) for highly dispersed concretes such as e.g. self-compacting concrete (SCC). Here, interaction between welan gum and two methacrylate ester-based polycarboxylate (PCE) superplasticizers was studied. It was found that the stabilizing effect of welan gum solely derives from its strong viscosifying effect on the aqueous phase of concrete (*i.e.* cement pore solution). The dispersing effectiveness of PCE is negatively influenced by this increased viscosity. A mechanistic study revealed that the stabilizer does not adsorb on cement and that it does not reduce adsorption of PCE. Thus, no competitive adsorption between the two admixtures occurs. This behavior differentiates welan gum from copolymerized VMAs based on AMPS® which adsorb on cement and can perturb PCE adsorption. When formulating SCC with welan gum as stabilizer, its dosage should be kept as low as possible to preserve the fluidity provided by PCE.

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## 1. Introduction

Self-compacting concrete (SCC), also referred to as self-consolidating concrete, is an extremely flowable, self-leveling and self-deairing concrete which generally contains a relatively high amount of powder constituents and a superplasticizer to provide such extremely high flowability [1]. SCC can be used for densely reinforced concrete structures (*e.g.* those with complex formworks) where vibration and compaction are difficult. However, in order to successfully formulate such powder-type SCC it has been found that accurate dosing of the admixtures and precise analysis of the moisture content present in the aggregates is mandatory. Therefore, some producers encountered difficulties to deliver an SCC of consistent high quality. As a consequence, an SCC incorporating a stabilizing agent as an additional admixture was developed [2,3]. The stabilizer (in literatures also referred to as viscosity modifying agent, VMA) provides coherence and anti-settling properties to the concrete. Such stabilized SCC exhibits a significantly higher tolerance for variations in the content of mixing water and therefore was found to be more practical in daily operations.

Generally, stabilizers for SCC consist of high molecular weight compounds such as welan gum, diutan gum, curdlan, hydroxypropyl cellulose, polyethylene glycol, and 2-acrylamido methane propane sulfonic acid (AMPS®)-based copolymers [4]. In Europe, AMPS®-based copolymers and welan gum are more prominent than any other kind of

stabilizer. Stabilizing admixtures are commonly used at much lower dosages (typically ~0.01–0.05% by weight of cement, bwoc) than the PCE superplasticizers present in the SCC formulation.

Welan gum, a microbial polysaccharide which is produced by aerobic fermentation using bacteria from the *Alcaligenes* species (ATCC-31555), presents a common VMA that can increase the yield stress and the shear thinning property of SCC while mitigating the effect of changes in the water content [5]. In contrast to cellulose-based VMAs, welan gum is less affected by temperature changes and does not negatively impact *e.g.* the air void system [6]. The main chain of welan gum consists of glucose units holding L-rhamnose or L-mannose as pendant groups. They shield the carboxylate group present in the backbone which forms a double helix [7]. Therefore, welan gum can impart high viscosity to alkaline solutions, even at significant concentrations of calcium ions [8–10]. The chemical structure of the welan gum is shown in Fig. 1.

Most chemical admixtures applied in concrete present anionic polyelectrolytes which physically adsorb onto positively charged surface sites of the cement particle, thereby developing their specific function (*e.g.* fluidifying, anti-bleeding, viscosifying, water retention, retardation, *etc.*) [11,12].

It has been reported before that the adsorption of superplasticizers (*e.g.* of PCEs) can be impeded by free sulfate anions present in the cement pore solution through a mechanism called “competitive adsorption” [13]. There, sulfate ions occupy the positively charged anchoring sites on cement, thus preventing the PCE from adsorbing in significant amount. In such case, the polymer can adsorb only on surface sites which are not occupied by sulfate, resulting in weak steric repulsion between the cement particles and low effectiveness. The phenomenon of

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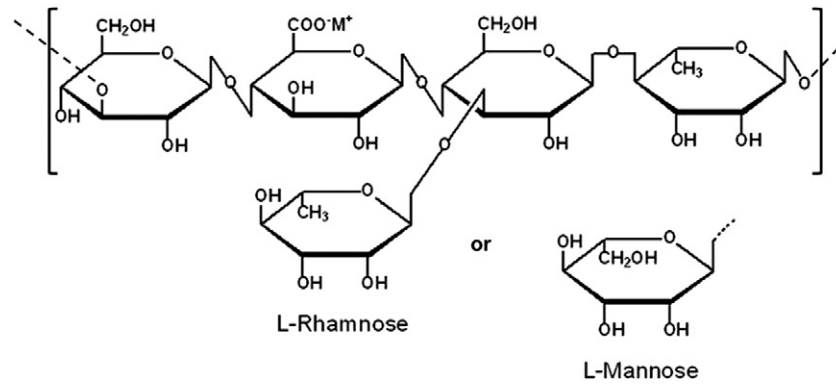


Fig. 1. Chemical structure of welan gum VMA [15].

competitive adsorption has been verified as well for the interaction between another type of VMA, a copolymer consisting of AMPS® and *N,N*-dimethyl acrylamide (NNDMA), and PCE [14]. Experiments revealed that the AMPS®-NNDMA stabilizer adsorbs on cement and therefore hinders the PCE to adsorb quantitatively, thus leading to lower fluidity. Fortunately, at increased dosages ( $>0.06\%$  bwoc) this kind of VMA starts to slightly disperse cement. This effect makes it possible to develop combinations of PCE and the AMPS®-NNDMA stabilizer which at the same time exhibit high fluidity and good coherence of the SCC at reasonable dosages of both admixtures.

Accordingly, it was speculated whether in SCC competitive adsorption between PCE and welan gum might occur as well. Two commonly used PCEs, i.e. one which is frequently applied in the precast concrete industry and possesses a high anionic charge, and another one which is used in ready-mix concrete and exhibits a low anionic charge, were synthesized and characterized with respect to their molecular properties and their adsorption behavior on cement. The impact of welan gum on the dispersing performance of the two PCE superplasticizers was determined *via* ‘mini slump’ testing and its influence on PCE adsorption on cement was quantified as well. From this data, compatibility between the PCE polymers and welan gum VMA was assessed and their mutual interactions were identified.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Cement

An ordinary Portland cement CEM I 52.5 N from HeidelbergCement, Geseke plant/Germany was utilized in this study. Its phase composition was determined *via* Q-XRD utilizing Rietveld refinement (see Table 1). The physical properties of this cement sample such as density, specific surface area (*Blaine*) and  $d_{50}$  value (average particle size) are also presented in Table 1. Particle size distribution was measured utilizing a laser granulometer (Cilas 1064; Cilas, Marseille, France), while the *Blaine* instrument used was from ToniTechnik, Berlin, Germany.

#### 2.1.2. Chemicals

Methacrylic acid (Sigma Aldrich, purity 99%),  $\omega$ -methoxy polyethylene glycol methacrylate ester macromonomer (PEG MA 2000 from Clariant, Burgkirchen/Germany, purity 98%), AMPS® monomer (Type 2402, Lubrizol, Wickliffe, OH; AMPS® is a registered trademark of the Lubrizol company), sodium peroxodisulfate (Merck Chemicals, purity 99%), 2-mercaptopropionic acid (Sigma Aldrich, purity 99%), NaOH flakes (Merck Chemicals),  $\text{NaNO}_3$  (Merck Chemicals, purity 99.5%), poly(diallyl dimethyl ammonium chloride) (polyDADMAC, Ciba Specialty Chemicals Ltd., Bradford, England), HCl (Merck Chemicals) and  $\text{D}_2\text{O}$  (Merck Chemicals, purity 99.9%) were used as obtained from the sources. Silica flour (SAA-1,  $d_{50} = 66 \mu\text{m}$ , quartz content  $\sim 98 \text{ wt.}\%$ )

was received from Halliburton, Celle, Germany while quartz flour (Quarzmehl,  $d_{50} = 24 \mu\text{m}$ , quartz content  $\sim 99 \text{ wt.}\%$ ) was supplied by Quarzwerke GmbH, Frechen, Germany.

#### 2.1.3. Welan gum VMA

An industrial powder sample of welan gum obtained from Hebei Henbo Biotechnology Co., Ltd. (Xinhe, Hebei Province, China) was used in this study.

#### 2.1.4. Polycarboxylate samples

Two methacrylic acid-*co*- $\omega$ -methoxy poly(ethylene glycol) (MPEG) methacrylate ester-based superplasticizers (denominated as 45PC2 and 45PC6) were synthesized and used in this study. Aqueous free radical copolymerization using sodium peroxodisulfate as initiator and 2-mercaptopropionic acid as chain transfer agent were employed in the synthesis. The general chemical structure of the PCE samples as well as a schematic representation to scale of their molecular architecture (calculation of molecular dimensions according to [16]) illustrating their different side chain densities is shown in Fig. 2. According to that, polymer 45PC6 is characterized by a long main chain and high anionic charge density whereas PCE 45PC2 exhibits a shorter main chain and a low anionic charge density. In the designations, ‘45’ refers to the number of ethylene oxide units ( $n_{\text{EO}}$ ) present in the side chain whereas ‘2’ and ‘6’ refer to the molar ratio between methacrylic acid and the methacrylate ester macromonomer. The two PCE copolymers were synthesized as follows: under nitrogen atmosphere, 80 mL of water was added to a 5 neck flask and heated to  $80 \text{ }^\circ\text{C}$  while stirring. To synthesize 45PC6, a solution A composed of 1.44 g mercaptopropionic acid, 105.6 g MPEG methacrylate ester macromonomer (55 wt.%)

Table 1

Phase composition and physical properties of the cement sample CEM I 52.5 N.

Phase or property	Content (wt.%) or value
$\text{C}_3\text{S}$ , monoclinic	52.0
$\text{C}_2\text{S}$ , monoclinic	27.6
$\text{C}_3\text{A}$ , cubic	4.4
$\text{C}_3\text{A}$ , orthorhombic	3.6
$\text{C}_4\text{AF}$ , orthorhombic	4.3
MgO	0.1
Free lime	0.1
$\text{CaSO}_4$	2.1
$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}^a$	0.7
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}^a$	0.4
$\text{K}_2\text{SO}_4$	0.5
$\text{CaCO}_3$	3.3
$\text{SiO}_2$	0.8
Loss on ignition (LOI)	1.9
Density ( $\text{g}/\text{cm}^3$ )	3.3
$d_{50}$ value ( $\mu\text{m}$ )	10.3
Specific surface area ( <i>Blaine</i> , $\text{m}^2/\text{g}$ )	0.33

<sup>a</sup> Determined *via* thermogravimetry.

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